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6. AUTHOR(S) Peter R. Ogilby			<div style="border: 2px solid black; padding: 5px; text-align: center;">DTIC SELECTED FEB 06 1994 F</div>	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry University of New Mexico Albuquerque NM 87131				
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13. ABSTRACT (Maximum 200 words) Spectroscopic experiments designed to better characterize excited-state interactions between oxygen and organic molecules (M) were performed. Data were recorded in both liquids and solid organic polymers. Problems of interest included (1) the effect of an applied magnetic field on the kinetics and yields of processes in the M-O ₂ photosystem, (2) the effect of changes in the M and O ₂ diffusion coefficients on both physical and chemical processes in the M-O ₂ photosystem, and (3) the effect of stabilizers used to inhibit polymer photodegradation on processes in the M-O ₂ photosystem.			<div style="font-size: 2em; font-weight: bold;">19950202 095</div>	
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Characterization of Excited State Oxygen-Organic Molecule
Complexes

Final Report

Peter R. Ogilby

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Statement of the Problem Studied:

Spectroscopic experiments designed to better characterize excited-state interactions between oxygen and organic molecules (M) were performed. Data were recorded in both liquids and solid organic polymers. Problems of interest included (1) the effect of an applied magnetic field on the kinetics and yields of processes in the M-O₂ photosystem, (2) the effect of changes in the M and O₂ diffusion coefficients on both physical and chemical processes in the M-O₂ photosystem, and (3) the effect of stabilizers used to inhibit polymer photodegradation on processes in the M-O₂ photosystem.

Summary of Results:

All results have been or will soon be published in journal articles. The list of these publications is provided on page 5. Outlined below are some important points.

1. Magnetic Field Effects.

The working hypothesis for this study was that the M-O₂ charge-transfer (CT) state could be influenced by the strength of an applied magnetic field. The radical cation of M and the radical anion of O₂ comprise this state, and thus both singlet and triplet spin states exist for this radical ion pair [^{1,3}(M⁺·O₂⁻)]. It was expected that the rate of singlet-triplet spin interconversion in the CT state would depend on the applied magnetic field strength, and, as a consequence, interconversions between lower lying states of the M-O₂ complex that have CT character would be influenced accordingly. For example, if the events that result in the spin forbidden transition M-O₂(a¹Λ_g) → M-O₂(X³Σ_g⁻) depend on the admixture of CT character, then the rate of M-induced

$O_2(a^1\Delta_g)$ deactivation should depend on the strength of the applied magnetic field. Furthermore, this effect should be more pronounced in polar media where the CT state is lower in energy and in more rigid media where the M- O_2 encounter pair lifetime is longer.

The experimental data supported the hypothesis. Magnetic field effects were indeed observed on the kinetics of several processes in the M- O_2 photosystem. Furthermore, these effects were more pronounced in polar and rigid (i.e., polymeric) media, thus implicating the CT state as the key intermediate that interacts with the applied field. These results indicate that photochemical processes of practical importance can be influenced by the strength of an applied magnetic field. Such processes include photoinduced oxygenation reactions that result in polymer degradation.

2. Oxygen Diffusion Coefficients in Organic Polymer Films.

We have developed a technique by which oxygen diffusion coefficients in polymer films can rapidly and accurately be quantified. Our method relies on spectroscopically measuring oxygen sorption into the film. Unlike existing techniques in which permeability through the film is measured, we are not susceptible to errors that arise from "pinholes" in the material. Furthermore, we directly measure the diffusion coefficient (D) rather than the permeability which is the product of D and the solubility (S) of the penetrant. We are able to decouple these two terms, obtaining S in a separate experiment. We are able to determine D over a large temperature range, which, in turn, yields the diffusion activation barrier.

We are interested in better understanding molecular events in a polymer film that both inhibit and facilitate oxygen diffusion. Our recent work has focussed on the effect of low molecular weight additives in both polystyrene and polycarbonate. We have particularly been interested in

trying to understand features of both the polymer and the additive that determine whether the additive acts as a plasticizer or anti-plasticizer. In a somewhat surprising result, we have ascertained that other gas molecules (e.g., nitrogen, argon, helium) will act as a plasticizer and facilitate the diffusion of oxygen in a given material.

Our studies in this area are expected to be useful to those interested in gas separation membranes, packaging materials, and protective coatings. In particular, we are able to comment on how such additive containing materials behave over a comparatively large temperature range.

3. Detection of $O_2(b^1\Sigma_g^+)$ in Solution.

The ground state of molecular oxygen is a triplet spin state ($X^3\Sigma_g^-$). The first excited state of oxygen is a singlet state ($a^1\Delta_g$). The photophysics and photochemistry of this latter state have been well studied. $O_2(a^1\Delta_g)$ is a well-known intermediate in many photooxygenation reactions. The second excited state of oxygen is also a singlet state ($b^1\Sigma_g^+$).

Prior to our study, almost nothing was known about the solution-phase (a) dynamics of $O_2(b^1\Sigma_g^+)$, and (b) photosensitized yields of $O_2(b^1\Sigma_g^+)$. The latter was viewed as being particularly important because $O_2(b^1\Sigma_g^+)$ is a precursor to $O_2(a^1\Delta_g)$.

In our study, we were able to spectroscopically detect $O_2(b^1\Sigma_g^+)$ in solution and monitor events that result in its (a) deactivation, and (b) formation in a photosensitized reaction.

List of Publications that Acknowledge ARO Support:

1. B. Wang and P. R. Ogilby, *J. Phys. Chem.*, **1993**, 97, 193-195. Quenching of $b^1\Sigma_g^+$ Oxygen in Solution. (Reprints have been sent to ARO)
2. P. R. Ogilby and J. Sanetra, *J. Phys. Chem.*, **1993**, 97, 4689-4694. Magnetic Field Effects on Excited State Oxygen-Organic Molecule Interactions. (Reprints have been sent to ARO)
3. B. Wang and P. R. Ogilby, *J. Phys. Chem.*, **1993**, 97, 9593-9598, Relative Fraction of Excited State Oxygen Formed as $b^1\Sigma_g^+$ in Solution Phase Photosensitized Reactions. (Reprints sent with this report)
4. R. D. Scurlock, D. O. Mártire, P. R. Ogilby, V. L. Taylor, and R. L. Clough, *Macromolecules*, **1994**, 27, 4787-4794. Quantum Yield of Photosensitized Singlet Oxygen ($a^1\Delta_g$) Production in Solid Polystyrene. (Reprints sent with this report)
5. Y. Kuriyama, P. R. Ogilby, and K. V. Mikkelsen, *J. Phys. Chem.*, **1994**, in press. Solvent Effects on the Oxygen-Organic Molecule Charge-Transfer Absorption.
6. Y. Gao, A. M. Baca, B. Wang, and P. R. Ogilby, *Macromolecules*, **1994**, in press. Activation Barriers for Oxygen Diffusion in Polystyrene and Polycarbonate Glasses: Effects of Low Molecular Weight Additives.
7. R. D. Scurlock, S. Nonell, S. E. Braslavsky, and P. R. Ogilby, *J. Phys. Chem.*, **1994**, in press. Effect of Solvent on the Radiative Decay of Singlet Molecular Oxygen ($a^1\Delta_g$).
8. P. R. Ogilby, M. Kristiansen, D. O. Mártire, R. D. Scurlock, V. L. Taylor, and R. L. Clough, *Adv. Chem. Ser.*, **1994**, in press. The Formation and Removal of Singlet ($a^1\Delta_g$) Oxygen in Bulk Polymeric Materials: Events That May Influence Photodegradation.
9. B. Wang and P. R. Ogilby, *J. Photochem. Photobiol.*, submitted for publication. Relative Fraction of Excited State Oxygen Formed as $b^1\Sigma_g^+$ in Solution Phase Photosensitized Reactions. 2. Effects of Sensitizer Substituent.

List of Participating Scientific Personnel:

Mr. Arthur Baca- Undergraduate student who has since gone on to graduate school at the University of Washington.

Mr. Bojie Wang- Graduate student who will receive his Ph.D. in the spring of 1995 on the basis of work completed as part of the ARO project.

Dr. Yasunao Kuriyama- Postdoctoral fellow who now has a position as an assistant professor of chemistry in Japan.

Dr. Jerzy Sanetra- Postdoctoral fellow who now has a position as an assistant professor of physics in Poland.

Dr. Rodger Scurlock- Postdoctoral fellow who is still a member of my group.